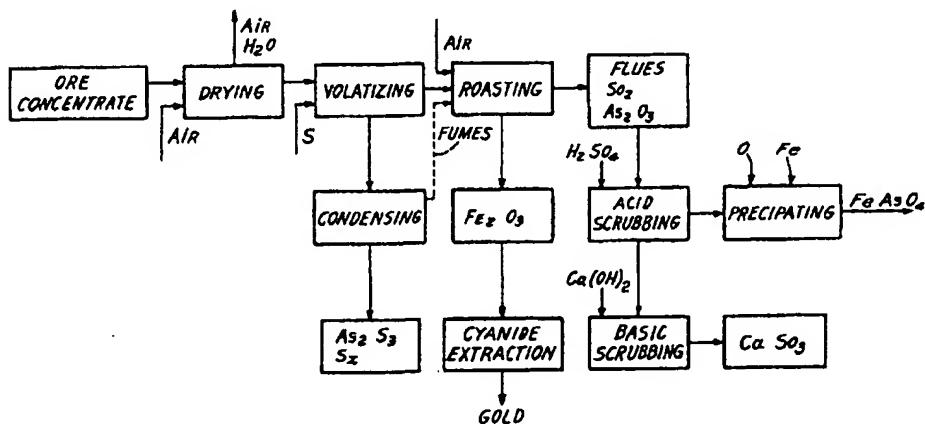




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(54) Title: PRECIOUS METAL RECOVERY FROM REFRACTORY SULPHIDIC ORES



(57) Abstract

A process for obtaining access to refractory gold and/or silver carried by arsenopyrites and/or arsenical pyrites comprises first heating dry ore concentrate containing arsenopyrites and/or arsenical pyrites at a temperature from 450 °C to 850 °C in an oxidizing atmosphere of sulfur devoid of free oxygen to volatile the larger part of arsenic from the starting ore and then roasting the non-volatile residue at a temperature of 850 °C or less leaving a residue of iron oxide substrate from which gold may be retrieved by cyanide extraction.

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TITLE OF THE INVENTION

PRECIOUS METAL RECOVERY FROM REFRACTORY SULPHIDIC ORES

FIELD OF THE INVENTION

5 The present invention pertains to a process for removing refractoriness in arsenical ore and, more particularly, to a process for obtaining access to refractory gold and/or silver carried by arsenopyrites and/or arsenical pyrites.

BACKGROUND OF THE INVENTION

10 Sulfide minerals are often associated with trace amounts of gold and silver. The recovery of these values from such ores is generally done by cyanide extraction applied on a concentrate of the sulfides obtained by flotation of the head ore.

15 With free gold dispersed in a sulfide, the cyanide extraction is a relatively simple operation that can achieve 95% recovery of the gold initially found in the head ore. However, under certain circumstances, the recovery can be as low as 5%; the gold is then said to be "refractory", that is, impossible to recover with standard cyanide extraction.

20 Such refractory gold is often associated with arsenopyrite (FeAsS). In such cases, gold exists more or less as a solid solution in the crystal lattice of the arsenopyrite and only by the total destruction of said lattice can it be recovered by cyanide extraction.

25 Since all the elements involved in the structure of arsenopyrite can be readily oxidized, the air roasting of the ore will destroy the arsenopyrite structure and will give access to gold as indicated by the following equation:

- 2 -



The air roasting of arsenopyrite has been often practised in the past in order to gain access to associated gold. However, for environmental reasons, such a process is now ruled out.

5 Gold bearing arsenopyrite being of relatively common occurrence, alternate means for the opening of the crystal lattice so as to gain access to gold has been considered. One technique calls for the pressure oxydation of the arsenopyrite with pure oxygen rather than air (R. M. G. S. Berezowski, D. R. Weir, "Pressure oxidation pretreatment of refractory gold",
10 Minerals and Metallurgical Processing Vol. 1 (May 1984), pp. 1-4).

With that process, since the reaction is performed in a pressure vessel at about 2 000 kPa with pure oxygen, there is no release of noxious arsenical compounds or sulfurous compounds. All of the arsenic ends up as insoluble ferric arsenate FeAsO_4 and all sulfur is discarded as sulfates.

15 However, the implementation of this technique is rated as being expensive because of the pressure operation at 200°C under acidic conditions and the consumption of pure oxygen.

20 Another approach calls upon bacterial degradation of the arsenopyrite. This operation works but is rated as being slow and sensitive to ore composition, traces of certain metals being inhibitors to bacterial action (P. B. Merchant, Fundamental and Applied Biohydrometallurgy, Elsevier Science Publishing, Amsterdam, 1986, pp. 53-76). Other techniques have been contemplated such as nitrate oxydation but are believed not to have reached the industrial pilot stage.

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It therefore appears that there is a need for a technology for the breakup of arsenopyrite that would be compatible with the environmental requirements associated with arsenic and sulfur, that would not incur the high capital and operation costs typical of pressure oxydation and that would show an improved kinetic when compared to biological degradation.

5

SUMMARY OF THE INVENTION

The present invention relates to a process conceived in such a way as to first separate and recover most of the arsenic fraction of gold-bearing arsenopyrites in the form of sulfides of arsenic.

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The process of the present invention therefore comprises the steps of:

15

heating dry ore concentrate containing arsenopyrites and/or arsenical pyrites at a temperature from 450°C to 850°C in an oxidizing atmosphere of sulfur devoid of free oxygen to volatize a high percentage of arsenic from the ore concentrate and leave a non-volatile residue including ferrous sulfides and remaining arsenic sulfide; and

roasting the non-volatile residue at a temperature of 850°C or less leaving a residue of iron oxide substrate from which gold may be retrieved by cyanide extraction.

20

The trace amount of arsenic remaining in the ore is then eliminated as ferric arsenide and the residual sulfur content of the ore, after removal of arsenic, is transformed into calcium sulfite. The end product after these two operations is a gold-bearing iron oxide and aluminosilicates readily amendable to cyanidation in order to collect gold.

In one preferred form, the process of the present invention includes the following steps:

- (a) the volatilization of arsenic in a sulfur-rich mildly oxidizing atmosphere, this step removing the larger part of arsenic

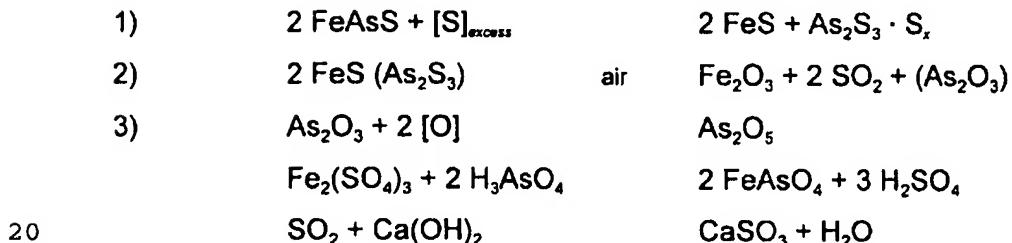
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- (b) the air oxidation of the residual material from the volatilization step so as to complete the removal of arsenic and the oxydation of remaining sulfur and iron; and

10

- (c) the acid scrubbing of arsenious oxide by an acid solution followed by basic scrubbing of SO₂ by a basic solution, the arsenious oxide being oxidized to arsenic oxide and precipitated as FeAsO₄.

The main steps of this process are illustrated by the following equations:



The implementation of those steps leads to a residual iron oxide that lends itself to easy and efficient gold recovery by cyanide extraction, a yield in the range of 95% being observed with an arsenopyrite ore which otherwise was not amendable to cyanidation.

25 Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating

- 5 -

preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

BRIEF DESCRIPTION OF THE DRAWING

5 Figure 1 is a block diagram detailing the various steps of the process.

DETAILED DESCRIPTION OF THE INVENTION

The conditions required for an optimal exploitation of the invention will now be described while referring to figure 1.

10 It should first be noted that the representation of the arsenopyrites by the formula "FeAsS" is a useful simplification; but the actual ores are generally much more complex than such an abstract structure might suggest. Very often, the arsenopyrite is associated with pyrite (FeS_2). Pending on the type of ore, sulfides of lead (galena) or zinc (sphalerite) or sulfides of base metals, such as copper and nickel, can also be present. The 15 following table gives a list of some of the volatile sulfides of arsenic that can be encountered in association with arsenopyrites.

<i>Table I</i> <i>Volatile sulfides of arsenic</i>		
Name	Formula	Boiling Temperature (°C)
Realgar	As_2S_2	565
Orpiment	As_2S_3	707
Sulfur	S_8	445

- 6 -

The concentrate obtained by flotation of the head ore is in the range of 80-90% in sulfides, the balance being made up of various silicates or aluminosilicates. This non-sulfurated fraction is carried along through the process.

5 It is known that arsenic sulfides are volatile entities as shown in Table I. Upon thermal treatment, in the absence of oxygen, it is possible to remove these volatiles components. However, in doing so, there must be enough sulfur present so as to make sure that the arsenic sulfides are volatilized in the form of the polysulfide $\text{As}_2\text{S}_3 \cdot \text{S}_x$, where "x" is of the order of
10 3 or more. To achieve this proper molecular ratio of sulfur to arsenic, pyrite, either already present or added to the ore, can play an important role by acting as a source of sulfur by the following reaction:



15 If the ore is still below a 3/1 ratio of S to As, even while taking into account the sulfur made available by decomposition of the pyrite, then elemental sulfur can be added so as to have the right proportion of these elements.

20 The interest of obtaining the arsenic in the form of a polysulfide is related to economical and environmental considerations. Arsenic polysulfides are essentially non-soluble entities with no vapor pressure at room temperature. Therefore, they can be stored or returned underground without creating environmental hazards. Also, these sulfides can be used readily as a source of arsenic in the manufacture of arsenical derivatives used as pesticides, preservatives for wood and similar products.

25 The volatilization of arsenic sulfide is done in a reverberatory type of furnace, in the absence of air. A relatively shallow layer of ore which has

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been previously dried is heated at a temperature of from 400 to 800°C and the arsenical vapors are driven off the furnace by the vapors of excess sulfur which acts as a carrier. Therefore, only initial purging with nitrogen at the start-up of the furnace is required.

5 Although air-free, the atmosphere in the furnace is mildly oxidizing because of the presence of excess sulfur. It is important that it never goes reductive since there would result a production of arsine (AsH_3), an exceedingly toxic gas with the smallest trace of water.

10 The volatiles from this treatment are directed to a condensation chamber where arsenic sulfides are condensed on large surfaces by internal cooling. Since the volume of gas circulation in the furnace is small, coming mainly from the volatilization of sulfur, the speed of circulation in the condenser will be very slow, allowing adequate exchanges with the condensing surfaces and solid growth rather than fine particle deposits.
15 Periodically, the condensed material is removed by scrapping. It will be readily noted that, from the boiling point of sulfur (445°C) and arsenic trisulfide (707°C), it is possible to separate the excess sulfur from the arsenic sulfide by the adjustment of the temperature of the condensing surfaces. This collected sulfur could be recycled to the system.

20 The boiling temperature reported for arsenic sulfide (As_2S_3) is 707°C at atmospheric pressure. At a lower temperature, say 500°C, there exists already a significant vapor pressure of arsenic sulfide but the rate of volatilization will be rather slow, particularly if the material is not swept by a gas in order to displace the vapors of the sulfide.

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If the temperature of the treatment is in the range of the boiling temperature of the arsenic sulfide, then the rate of volatilization will be much faster, and the large volume of gas thus generated will sweep out the sulfide.

5 This is why a temperature range of 700-750°C is preferred although some volatilization already takes place at 450°C.

Above the preferred range of 700-750°C, additional temperature expands further the gaseous sulfide, thus speeding its evacuation, but a significant increase in energy consumption is involved.

10 The non-volatile fraction at the end of the volatilization of arsenic compounds is essentially ferrous sulfide (FeS) with the non-sulfurated products initially present in the dried concentrate.

Arsenical compounds are substantially removed, to the extent of 95% or more, by volatilization. The relatively small amount remaining is handled in the course of the second step of the process.

15 The non-volatile fraction is then oxidized with air, in a closed rotary kiln, so as to transform all the sulfur into sulfur dioxide and the trace amounts of arsenic into arsenious oxide, As₂O₃.

20 It must be noted that this oxidation reaction is an exothermic process. It is important to keep an adequate control over the temperature during this roasting. If maximum oxidation speed is allowed by unlimited access of air (dead burning), the resulting product will show significant sintering and will not perform correctly when submitted to cyanide treatment for the recovery of gold; it will still be somewhat refractory. But if air access to the roaster is controlled in such a way that the temperature during the

roasting does not exceeds 850°C, then the resulting ferric oxide has a very open structure and the recovery of gold from this burned fraction reaches 95%.

5 The non-condensed gases from the distillation of arsenic sulfides along with the flues from the roasting of ferrous sulfide are directed first to a scrubbing tower operated under slightly acidic conditions, by addition of some sulfuric acid, so as to prevent significant solution of SO₂ (pH around 2.5).

10 In that tower, any arsenical material carried over from the distillation to the roasting is dissolved as trivalent arsenious oxide and then precipitated by addition of a ferric salt after oxydation to arsenic oxide to give ferric arsenate. Ferric arsenate is a very stable and completely insoluble salt of arsenic that can be disposed in the environment without problem.

15 Under acidic conditions, the SO₂ resulting from the roasting operation will not be dissolved because of the low pH in the first scrubber but will be carried over to a second scrubbing tower operated with a lime slurry. Under such conditions, SO₂ will be precipitated as calcium sulfite, an insoluble salt.

20 The roasted ore can then be submitted to standard cyanide extraction for gold and the residual solids disposed of along with the ferric arsenate and calcium sulfite.

25 Hence, the present invention leads to the transformation of a refractory arsenopyrite into a material from which gold can be reclaimed without problem. This process operates at atmospheric pressure and allows the recovery of most of the arsenic as a source of useful products rather than

- 10 -

waste and its operation is entirely compatible with environmental regulations concerning arsenic and sulfur.

EXAMPLE

5 *Kassandra* arsenical material containing 40% Fe, 41% S, 12% As, 0.8% Zn, 0.08% Cu, 0.54% Pb, 25.5 g/t Au and 20 g/t Ag is extremely refractory since a cyanide extraction with 0.5 Kg NaCN/t of ore, a standard cyanide procedure operated at pH 10.5, gave a recovery of 7% of the gold present.

10 By application of the present invention, the material was first treated at 730°C in the absence of air so as to let the volatile arsenic sulfides evaporate.

The residual material was then oxidized by a slow air stream, the temperature in the reacting mass being at 830-850°C.

15 After cooling, the residual product was submitted to cyanide extraction using 0.5 Kg/t of cyanide per treated ore at pH 10.5.

The recovery of gold from the initial sample was 95%.

The arsenic condensates were treated with hydrogen peroxide and the arsenic precipitated by addition of ferric sulfate to give the expected ferric arsenate.

20 Although the invention has been described above with respect with one specific form and one example, it will be evident to a person skilled in the art that it may be modified and refined in various ways. It is therefore

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wished to have it understood that the present invention should not be limited in scope, except by the terms of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for obtaining access to refractory gold and/or silver carried by arsenopyrites and/or arsenical pyrites comprising the steps of:

heating dry ore concentrate containing arsenopyrites and/or arsenical pyrites at a temperature from 450°C to 850°C in an oxidizing atmosphere of sulfur devoid of free oxygen to volatize a high percentage of arsenic from said ore concentrate and leave a non-volatile residue including ferrous sulfides and remaining arsenic sulfide; and

roasting said non-volatile residue at a temperature of 850°C or less leaving a residue of iron oxide substrate from which gold may be retrieved by cyanide extraction.

15

2. A process as defined in claim 1, wherein said roasting step is conducted in an air oxydizing atmosphere.

20 3. A process as defined in claim 2, further comprising the step of condensing said high percentage of arsenic volatized to recover arsenic polysulfide and an excess of elemental sulfur.

25 4. A process as defined in claim 3, wherein non condensed fumes from said condensing step are directed to said roasting step.

5. A process as defined in claim 1, wherein flues obtained from said roasting step are circulated to an acid scrubber to dissolve arsenious oxides.

6. A process as defined in claim 1, wherein said sulfur oxides obtained from said roasting step are further circulated to a second scrubber to transform said sulfur oxides into insolubles sulfites or sulfates of calcium.

5

7. A process as defined in claim 5, wherein said arsenious oxides are oxydized to arsenic oxides and precipitated as ferric arsenate.

10
10

8. A process as defined in claim 1, wherein said ore concentrate is air dried, prior to said volatization step, at a temperature of about 100°C to 150°C.

15

9. A process as defined in claim 1, wherein said volatization step is done by reverbatory heating a shallow layer of ore concentrate.

20

10. A process as defined in claim 1, wherein said roasting step is carried out in a temperature controlled rotary kiln.

25

11. A process as defined in claim 1, wherein air access to said roasting step is controlled to limit the roasting temperature to 850°C or less.

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12. A process as defined in claim 6, wherein the second scrubbing step is operated with a lime slurry.

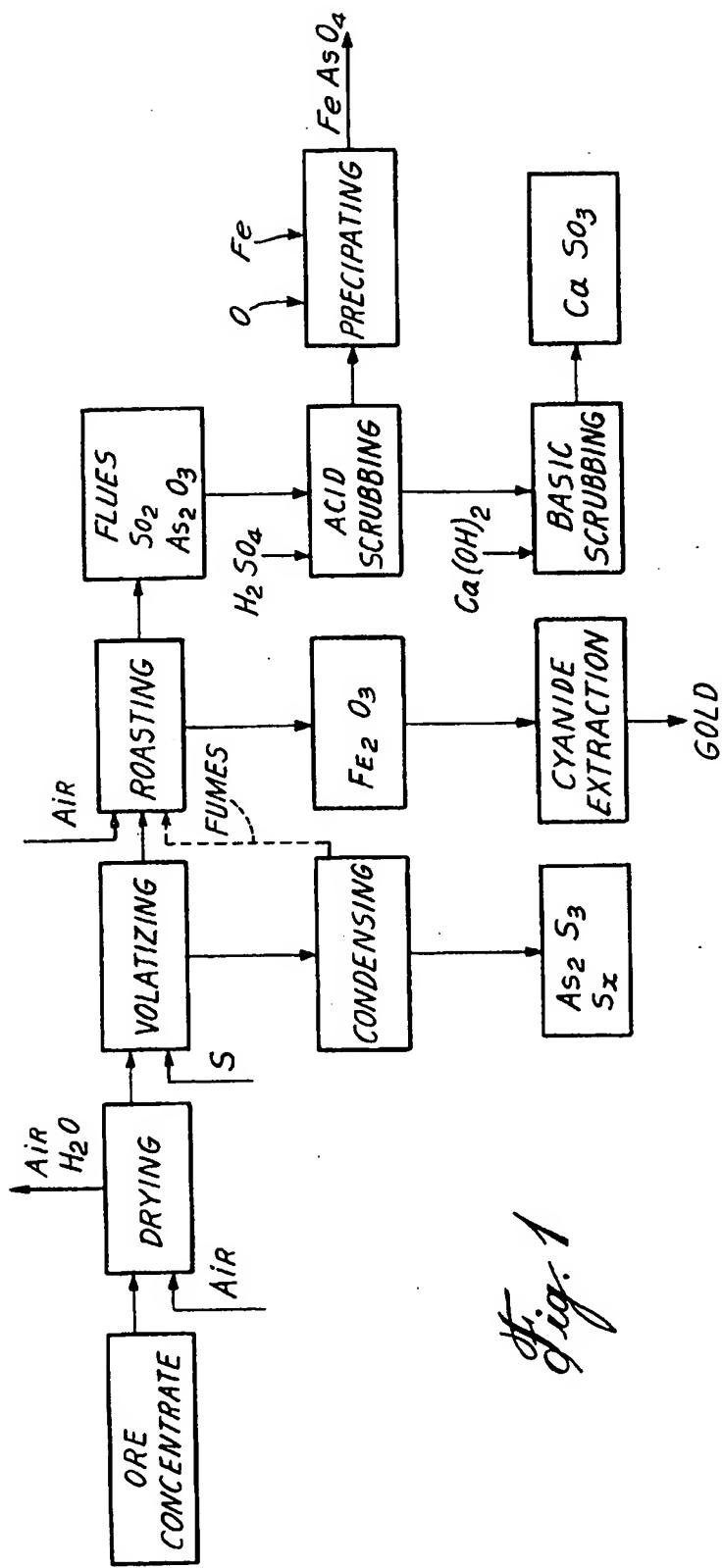


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 96/00547

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C22B1/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C22B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>MINERALS AND METALLURGICAL PROCESSING, May 1984, LITTLETON, US, pages 1-4, XP000196557</p> <p>BEREZOWSKY R M G S ET AL: "PRESSURE OXIDATION PRETREATMENT OF REFRACTORY GOLD" cited in the application</p> <p>---</p>	
A	<p>MARCHANT P B: "COMMERCIAL PILOTING AND THE ECONOMIC FEASIBILITY OF PLANT SCALE CONTINUOUS BIOLOGICAL TANK LEACHING AT EQUITY SILVER MINES LIMITED", FUNDAMENTAL AND APPLIED BIOHYDROMETALLURGY, VANCOUVER, AUG. 21 - 24, 1985, VOL. 4, PAGE(S) 53 - 76, LAWRENCE R W; BRANION R M R; EBNER H G XP000608352</p> <p>cited in the application</p> <p>Publisher: ELSEVIER, Amsterdam-Oxford-New York-Tokyo, 1986</p> <p>---</p> <p>-/-</p>	

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 96/00547

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	GB 755 259 A (INSTITUTO NACIONAL DE INDUSTRIA) 22 August 1956 see claims 1-5 ---	1
A	GB 755 344 A (INSTITUTO NACIONAL DE INDUSTRIA) 22 August 1956 see claim 1 ---	1
A	GB 2 188 943 A (CAPPER PASS LIMITED) 14 October 1987 see claim 1 ---	1
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A	DE 32 27 063 A (KLÖCKNER-HUMBOLDT-DEUTZ) 26 January 1984 see page 4, line 14 - page 5, line 2 -----	5-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Appl. No

PCT/CA 96/00547

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